

Investigation of
2,4-Dinitrophenylhydrazine Impregnated
Adsorbent Tubes for the Collection of
Airborne Aldehydes

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INVESTIGATION OF 2,4-DINITROPHENYLHYDRAZINE
IMPREGNATED ADSORBENT TUBES FOR THE
COLLECTION OF AIRBORNE ALDEHYDES

by

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate environmental problems; to support regulatory actions by developing an in-depth understanding of the nature of processes that affect health and the ecology; to provide innovative means of monitoring compliance with regulations; and to evaluate the effectiveness of health and environmental protection efforts through monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, has responsibility for assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air and Radiation, the Office of Toxic Substances, and the Office of Solid Waste.

The determination of the identities and concentrations of airborne aldehydes in indoor/outdoor environments is an area of increasing significance to EPA. The evaluation and intercomparison of sampling techniques which can provide information on concentration levels of these pollutants is an important step in developing the tools needed to address health and environmental issues. This report describes an investigation of techniques which utilize 2,4-dinitrophenylhydrazine derivatizing reagent to facilitate sampling and analysis of airborne aldehydes.

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ABSTRACT

The objective of this study was to investigate the use of 2,4-dinitrophenylhydrazine (DNPH) impregnated adsorbents for sampling airborne aldehydes. Investigation focused primarily on the Sep-Pak C18 adsorbent material because it has been used in the past by researchers to sample airborne aldehydes and it is available as a commercially prepared cartridge. Experimental results using a 17 m³ environmental chamber and various spiked amounts of aldehyde material (low ppb levels) showed that the DNPH-coated cartridge and the DNPH/acetonitrile impinger methods gave equivalent results. Blank levels of the DNPH-coated cartridges were studied as a function of storage time using various containers and temperature conditions. Canisters pressurized with zero-grade nitrogen provided the best storage device. Lower blank levels were also obtained when the cartridges were stored at lower temperatures. Blank levels appear to equilibrate after six days of storage. Significant batch-to-batch differences in blank levels were observed. To assure that quality data will be obtained, cartridges should be grouped according to batch number and blank levels should be determined prior to any field monitoring effort. Blank cartridge levels should be an order of magnitude lower than the sample cartridge level. Adjustment in sampled volume should be made accordingly. High performance liquid chromatography with UV detection proved to be a sensitive and stable analytical method for the DNPH derivatives. Three laboratories employing the above sampling and analysis methodology reported similar results after analyzing an eight component aldehyde derivative standard (2 ng/ μ l). Results of field sampling demonstrated that low ppb levels of airborne aldehydes can be determined with good analytical precision.

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SECTION 1

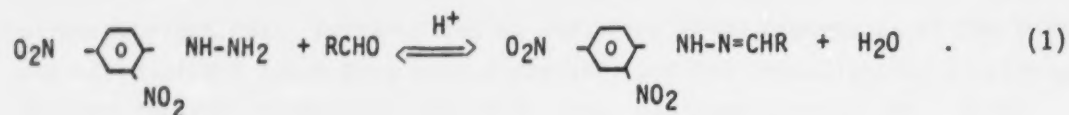
INTRODUCTION

The determination of aldehydes and other carbonyl compounds in the atmosphere is of interest because of their importance as precursors in the production of photochemical smog, as photochemical reaction products and as a major source of free radicals in polluted environments. Additionally, short-term exposures to aldehydes such as formaldehyde, acetaldehyde, acrolein and crotonaldehyde are known to result in irritation of the eyes, skin and mucous membrane of the upper respiratory tract (1).

These carbonyl species are emitted into the atmosphere either directly from certain industrial processes or as secondary products from combustion sources. In rural areas, concentrations of 0.6 to 1.3 ppb formaldehyde have been reported (2). In urban environments, formaldehyde levels range from several ppb to over 50 ppb depending upon location and meteorological conditions (3-5). Tanner and Meng (3) have reported acetaldehyde levels 20 to 50 percent of formaldehyde concentrations. Grosjean (4) has noted similar acetaldehyde/formaldehyde ratios. Very little ambient air data exist, however, for the other carbonyl species.

The limited amount of speciated aldehyde data is largely due to the lack of a simple, sensitive, and selective analytical method. Derivatization techniques utilizing 2,4-dinitrophenylhydrazine (DNPH) reagent are currently being evaluated and will likely replace the earlier analytical methods--chromatropic acid (6), pararosaniline (7), and direct analysis via gas chromatography (8). With the DNPH technique, a derivative is formed by the reaction of DNPH with the carbonyl compound in the presence of acid to form the corresponding hydrazone derivative.

Equation 1 shows the reaction for aldehydes:



Initially, the DNPH derivatives were separated and identified using packed column gas chromatographic techniques (9). More recently, high performance liquid chromatography (HPLC) has been employed by researchers to more easily separate and elute the DNPH derivatives (10,11). Quantitation of the hydrazone derivatives using HPLC is accomplished with a UV detector.

Sampling for carbonyl species is generally accomplished with either impinger or solid adsorbent techniques. With impinger methods, aqueous or organic solvents (or mixtures of both) have been used to prepare the DNPH absorbing solution. The use of DNPH/acetonitrile solutions as reported by Kuntz et al. (10) and Lipari and Swarin (11) permit the direct analysis of the absorbing solution using reversed phase HPLC. The DNPH/acetonitrile impinger technique has simplified sampling efforts, but it is not ideally suited for extended sampling periods (solvent evaporation) nor for field use when samples containing DNPH derivatives/solvent are to be stored and shipped to a central laboratory for analysis.

The use of adsorbent traps coated with DNPH circumvents some of the short-comings of the impinger technique. Adsorbents that have been impregnated with DNPH include XAD-2, silica gel, glass beads and glass fiber filters. Kuwata et al. (12) and Tejada (13) used prepacked plastic cartridges (Sep-Pak C18) and coated them with acidified DNPH solution to determine ambient air and source levels of carbonyl species. Lipari and Swarin (14) employed prepacked Florisil cartridges (Thermosorb/F) and coated them with DNPH (not acidified) to measure formaldehyde concentrations in similar air matrices. Tejada (15) further showed equivalent results for most carbonyl species when comparing the impregnated cartridge method with the DNPH/acetonitrile impinger sampling system. He has also provided standard operating procedures for coating the cartridges, for conducting sampling, and for analyzing the collected material.

Other than Tejada's work (15), detail documentation of sampling and analytical procedures is sparse. The current study has been undertaken to further investigate the use of DNPH impregnated adsorbents for sampling airborne aldehydes. Proper clean up and preparation procedures of the DNPH coated adsorbent tubes have been discussed, and the investigation of storage devices for the impregnated adsorbent tubes has been carried out. Three analytical methods have also been examined during the study. The HPLC method served as the primary analytical tool and was compared with a gas chromatographic technique to determine relative selectivity and sensitivity of each. A third method, a continuous monitoring formaldehyde analyzer, was tested for its selectivity and sensitivity for that compound.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of this work, it is concluded that the DNPH-coated Sep-Pak cartridges provide the researcher with a simple yet accurate means for sampling airborne aldehydes. Furthermore the analysis of the hydrazone derivatives is facilitated by the use of high performance liquid chromatographic methodology. Specific conclusions and recommendations are given below:

- (1) Experimental results using a 17 m³ environmental chamber and various spiked amounts of aldehyde material showed that the DNPH-coated Sep-Pak cartridge and the DNPH/acetonitrile impinger methods gave equivalent results. Cartridge/impinger ratios ≥ 0.85 were obtained for most of the tested aldehydes (acrolein ratio = 0.74). Based on the calculated chamber concentrations, both sampling methods showed absolute recoveries greater than 80 percent for formaldehyde, acetaldehyde, butyraldehyde and benzaldehyde. Considering the generated concentration levels and the adsorptive nature of these compounds, the above absolute recovery is quite acceptable. However for acrolein, recoveries ranged from 28 to 44 percent. For crotonaldehyde, recoveries of 127 to 159 percent were found. Both compounds are olefinic aldehydes and it is likely that these species undergo additional chemical reactions during the sampling and analysis process. We do not recommend using the cartridge sampling approach for these two carbonyl species.
- (2) Blank levels of the DNPH coated Sep-Pak cartridges were investigated as a function of storage time using various containers and temperature conditions. Canisters pressurized with nitrogen provided the best storage device. Storage in a refrigerator or freezer also resulted in lower blank levels than storage at room temperature. Coated cartridges showed no detectable amount of the aldehyde derivatives when analyzed within several hours of preparation. However, we found measurable levels after six days of storage. Blank levels did not appear to increase significantly after the sixth day. During these tests,

several different batches of the Sep-Pak cartridges were housed within the same storage device. We observed an eight-fold difference in blank levels. This batch-to-batch difference may significantly affect the quality of data collected during a monitoring study. To assure that quality data will be obtained, cartridges should be grouped according to batch number and blank levels should be determined prior to any field monitoring effort. We recommend that the blank cartridge level be an order of magnitude lower than the sample cartridge level. For instance, a formaldehyde concentration of 1 ppb converts to 8.59 ng/L (formaldehyde-DNPH derivative @25°C and 1 atm). For a sampled volume of 100 liters, this amount corresponds to a cartridge loading of 859 nanograms. If 5 ml solvent is used to extract the derivative from the cartridge and a 10 μ l aliquot of the mixture is injected onto the HPLC, then ~1.7 ng will be measured. Based upon our recommendation, the cartridge blank level should be 0.17 nanograms or less per injection (or 85.9 ng per cartridge).

- (3) High performance liquid chromatography was shown to be a sensitive and stable analytical method for the hydrazone derivatives. Very good precision was obtained from the analyses of an eight component standard (2 ng/ μ l) over a two month period. Although gas chromatography methods were also examined and gave better sensitivity, a considerable number of extraneous peaks prohibited acceptable identification and quantitation of the aldehyde derivatives.
- (4) Good interlaboratory agreement was obtained from the analysis of an eight component standard (2 ng/ μ l). These results demonstrate that the hydrazone derivatives can be prepared accurately at the lower ng/ μ l level and are stable in solution for at least four months.
- (5) Aldehyde samples collected at a suburban location showed good analytical precision and low blank levels. These results demonstrate that low ppb levels of airborne aldehydes can be determined with the sampling and analysis methodology discussed in this report.
- (6) A continuous monitoring analyzer was evaluated and exhibited good sensitivity and selectivity for formaldehyde. The unit was able to detect > 8 ppb formaldehyde and was nonresponsive to ppb levels of other aldehydes.

SECTION 3

EXPERIMENTAL

INSTRUMENTATION

A Varian model 5000 liquid chromatograph coupled to a LDC model 1203 uv (360 nm) detector was used as the primary analytical tool. The instrument was equipped with an automatic sampler (10 μ l sample loop). HPLC peak separation was accomplished with two DuPont Zorbax ODS columns (4.6 mm by 25 cm) connected in series. Acetonitrile/H₂O mixture (65/35) served as the mobile phase. Column flow was 0.8 ml/min. Peak areas were determined with a Hewlett Packard model 3392 integrator.

Gas chromatographic analyses were carried out with a Hewlett Packard model 5890 instrument. The instrument was equipped with flame ionization and electron capture detectors. Peak separation was achieved with the aid of an OV-1 megabore fused silica capillary column (30 m by 0.50 mm). Column flow was set to 10 ml/min (zero grade helium). The column oven was programmed from 190°C to 250°C at 8°C/min. Peak quantitation was accomplished with a Hewlett Packard model 3392 integrator.

A model TGM 555 formaldehyde analyzer from CEA Instruments, Inc., was evaluated for its sensitivity and selectivity toward formaldehyde. The instrument incorporates the methodology developed by Lyles et al. (16). Formaldehyde in air is absorbed in a sodium tetrachloromercurate solution that contains a fixed quantity of sodium sulfite. Acid bleached pararosaniline is added, and the intensity of the resultant dye is continuously measured with a photodetector (550 nm).

REAGENTS

The following reagents were used for this study:

- 2,4-dinitrophenyl hydrazine (DNPH) - Aldrich Chemical, reagent grade
- Acetonitrile (ACN) - Burdick and Jackson, UV grade

- Water - distilled, 0.2 μm filtered, degassed
- Sulfuric acid - analytical grade
- Hydrochloric acid - analytical grade
- Methanol - Burdick and Jackson, UV grade
- Aldehydes for preparation of DNPH derivative standards - Aldrich Chemical, >98 percent purity
- Carbonyl standards - as 2,4-DNPH derivatives prepared as described later
- Sep-Pak silica gel cartridges - Waters Associates
- Maxi-clean cartridges - Alltech Associates.

PROCEDURES

Purification of DNPH Reagent

The DNPH reagent was purified by boiling an excess amount of DNPH in 200 ml of ACN (saturated solution). The supernatant liquid was transferred to a beaker, covered with a watch glass and allowed to cool slowly. This cooling step maximized the crystal size and purity. After cooling, the beaker was put into an ice bath to complete the crystallization. The remaining liquid was decanted and discarded. Then the crystals were washed twice with 60 ml of ACN, transferred to another beaker, 200 ml of ACN was added, and the above process was repeated. After the second recrystallization step, the crystals were filtered and transferred to a small vial. The vial was heated to 50°C and the crystals were dried with a clean nitrogen gas stream. The vial was sealed with a screw cap containing a Teflon insert. To minimize passive adsorption of airborne carbonyl species, the crystals were stored in a charcoal filled can in a refrigerator. To check the purity of the crystals, 0.06 g was weighed out and dissolved in 250 ml of ACN. Fifty μl of sulfuric acid was added. This solution was analyzed by HPLC. The crystallization process should be repeated if HPLC analyses show the presence of aldehyde-DNPH derivatives greater than 0.1 ng/ μl .

Preparation of Stock DNPH Reagent

DNPH crystals (0.06 g) were weighed out and dissolved in 250 ml of ACN. Fifty μ l of sulfuric acid was added. This solution was stored in an amber bottle in the refrigerator.

Preparation of Carbonyl-DNPH Derivatives

The individual aldehyde (100 μ l or 300 μ l for a 37 percent formaldehyde solution) was added to a saturated solution of DNPH in 60 ml of 2N HCL. The colored precipitate was filtered and washed with 2N HCL and water. The precipitate was transferred to a small screw cap vial and dried with a clean nitrogen gas stream (@ 50°C).

Chromatographic purity was checked by preparing a 2 mg/L standard of each derivative in ACN and analyzing by HPLC. The derivative should be recrystallized in methanol if the purity level is unsatisfactory.

Preparation of Standards

Standard stock solutions (20 mg/L) were prepared by dissolving ~0.002 g of the individual derivative in 100 ml of ACN. All stock solutions were contained in glass screw cap vials with Teflon cap liners and stored in a refrigerator. The working calibration standard (2 mg/L) was prepared by combining 5 ml of each derivative and bringing solution to 50 ml with stock DNPH/ACN. The working standard was stored in a screw cap vial with a Teflon cap liner and housed in a refrigerator when not in use.

Preparation of Adsorbent Tubes for Sampling

The sampling end of the adsorbent tube was connected to a 10 ml glass syringe (without the barrel) and the syringe was placed in a syringe rack (Figure 1A). Ten ml of ACN was added to the syringe and allowed to drain through the tube into a waste beaker. Air bubbles between the syringe and the tube were removed with ACN by using a disposable Pasteur pipet. After the ACN rinse had completely drained through the tube, 7 ml of the stock DNPH reagent was added to the syringe. Air bubbles again were displaced using a Pasteur pipet. The reagent was allowed to gravity feed through the tube until the flow stopped at the other end. Excess liquid clinging to the tube was dabbed off with a clean tissue.

Figure 1A

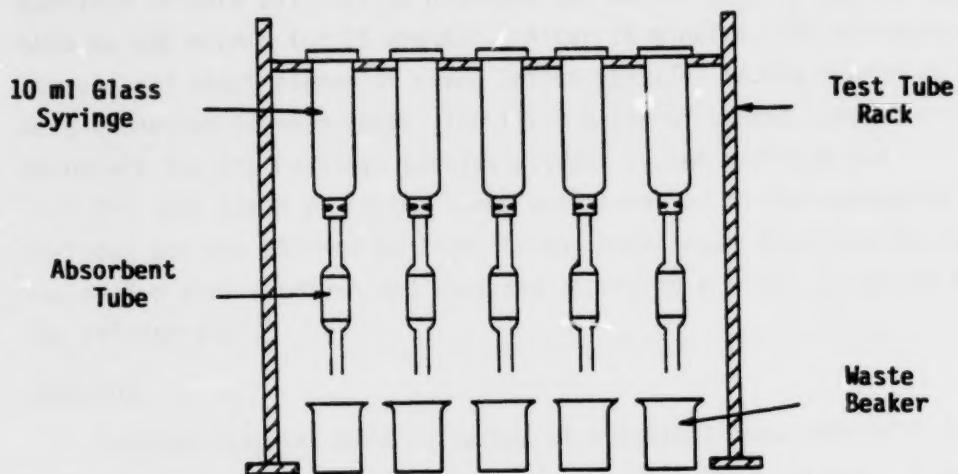


Figure 1B

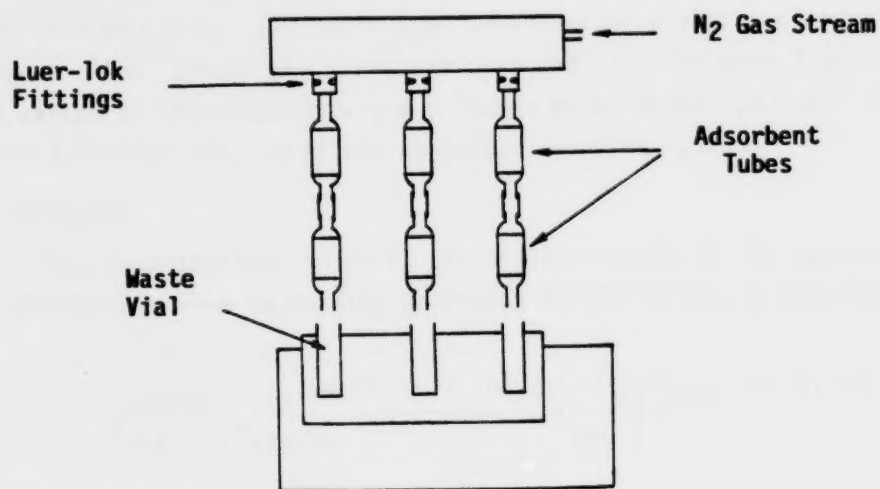


Figure 1A and 1B. Diagram of the coating (Figure 1A) and drying (Figure 1B) apparatus used to prepare the Sep-Pak cartridges for sampling airborne aldehydes.

Following the above coating procedure, the first batch of tubes was removed from the syringes and connected to the Luer ports of a drying manifold (Figure 1B). Clean nitrogen gas was allowed to pass through each tube at 300 ml/min for 15 minutes. After 15 minutes, the nitrogen flow was stopped and short pieces of clean Teflon FEP 1/4" tubing flared at both ends were connected to each tube. The first batch of coated tubes served as scrubbers for any carbonyl species present in the nitrogen gas.

The next batch of coated tubes was connected to the scrubbers and nitrogen gas was allowed to flow through each one. After drying, each tube was sealed with aluminum end caps and stored in a glass stoppered bottle in the refrigerator.

Sampling

Impinger samples were collected at a nominal flow rate of 1 L/min using a single impinger containing 10 ml of the stock DNPH reagent. A second impinger filled with silica gel protected downstream elements from acetonitrile. The sample flow was directed through a rotameter, pump, and wet test meter assembly.

Cartridge samples were collected at nominal flow rates ranging from 0.06 to 0.80 L/min. The cartridges were sampled either individually or in tandem. Flow through the tubes was directed to Tylan mass flow controllers and vented to the atmosphere via a Thomas model diaphragm pump. Figure 2 shows a typical diagram of the cartridge sampling system.

Calculations

The concentrations in parts per billion (ppbV) of the carbonyl species in ambient air were calculated according to the following equation:

$$C(\text{ppbV}) = \frac{A_{\text{sample}}}{A_{\text{std}}} \times \frac{C_{\text{std}} (\mu\text{g/ml})}{V_{\text{sampled}} (\text{L})} \times \frac{VE (\text{ml})}{MW} \times \frac{T}{T_{\text{std}}} \times \frac{P_{\text{std}}}{P} \times \frac{22.4 \text{ L/mole}}{10^3}$$

where:

C = concentration of aldehyde (ppbV)

A_{sample} = peak area of aldehyde derivative in sample solution

A_{std} = peak area of aldehyde derivative in standard solution

C_{std} = concentration of aldehyde derivative in standard solution

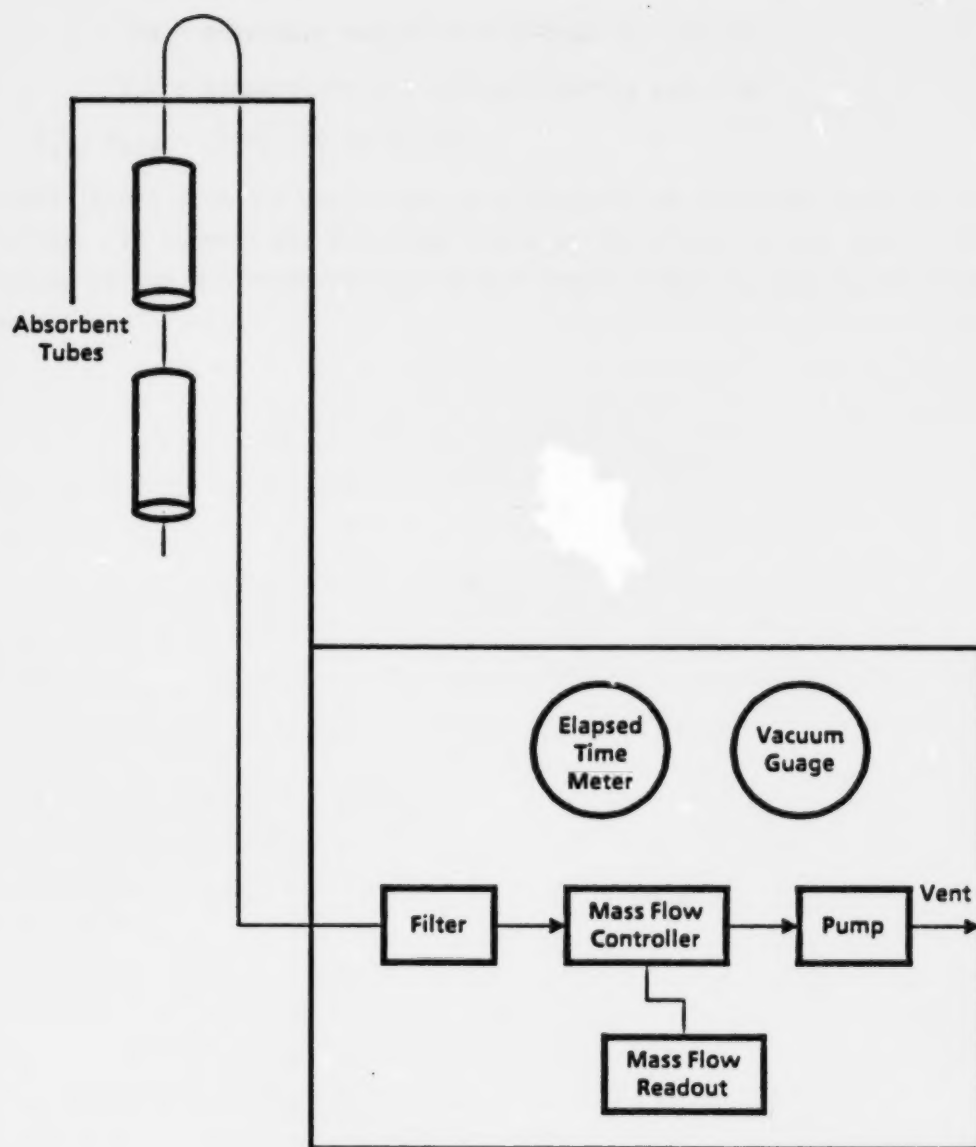


Figure 2. Diagram of adsorbent sampling device for airborne aldehydes.

V_{sampled} = volume of air sampled (@ T and P)

V_E = volume of acetonitrile used in extraction

MW = molecular weight of aldehyde derivative

T,P = temperature and pressure during sampling

$T_{\text{std}}, P_{\text{std}}$ = 273°C, 29.92 in. Hg.

Blank levels from the cartridges were reported as nanograms injected on-column. To convert the nanogram levels of the blanks to ppb levels, the volume of air processed through actual sample tubes is used in the above equation.

SECTION 4

RESULTS AND DISCUSSION

INVESTIGATION OF ANALYTICAL METHODOLOGY

Three analytical methods were utilized during the study. The HPLC/UV method served as the primary analytical tool during the experimental phase of the study. The GC method was employed to determine if better selectivity and sensitivity for the hydrazone derivatives could be achieved. The third method, a continuous monitoring analyzer, was tested for its selectivity and sensitivity for formaldehyde.

HPLC/UV Method

Figure 3 shows a chromatogram from one of the analyses of a working standard containing 1-2 ng/ μ l of eight hydrazone derivatives. Chromatographic conditions were optimized for the separation of acrolein, acetone, and proprionaldehyde derivatives. The chromatogram shows that acceptable resolution of the eight compounds is obtained with the specified operating conditions. A 10 μ l sample injected on column corresponds to ~20 ng of each component (10 ng of formaldehyde). For this amount of material, an integrator signal to noise ratio of 100 to 1 is obtained. Results from repeated analyses of the eight component standard over a two month period are shown in Table 1. Nine analyses were compared over this time period. Statistical treatment of the data revealed excellent analytical precision with standard deviation values ranging from 1.4 to 4.0 percent.

Relative response factors (RRF) for the hydrazone derivatives are shown in Table 2 (formaldehyde derivative = 1.00). Since the UV detector responds to the aromatic structure of the derivatives, we would expect to obtain similar response factors (assuming that the derivatives were weighed out accurately). For most of the derivatives, RRF values close to one are obtained. The RRF for acrolein, however, is 1.28, while the factor for acetone is 0.79. We suspect that their deviation from one may be due to

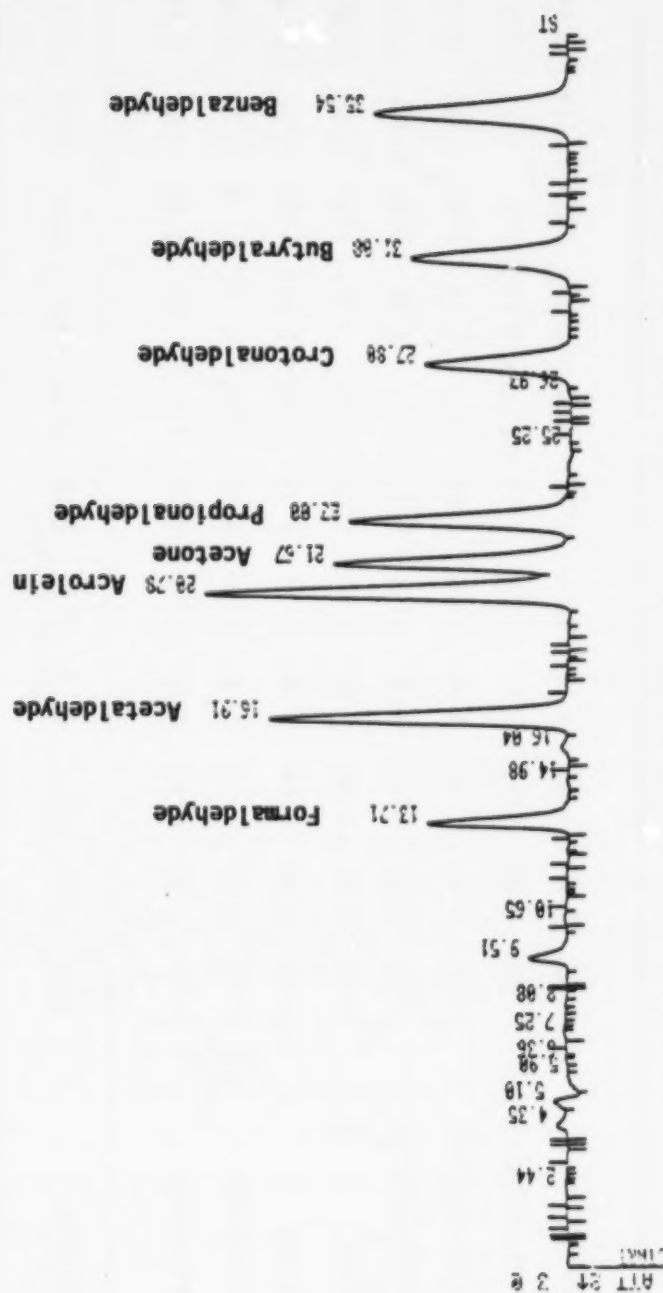


Figure 3. Chromatogram from the injection of 10 μ l of the working standard of eight DNP-derivatives in acetonitrile (1 to 2 ng/ μ l). LC operating conditions are specified in the text.

TABLE 1. RESULTS FROM THE ANALYSIS OF AN EIGHT COMPONENT STANDARD OVER A TWO MONTH PERIOD

Compound*	Analysis Date										Mean	S.D.	% S.D.
	4/27	4/29	5/1	5/13	5/14	5/18	5/28	6/3	6/15				
Formaldehyde	1.11	1.00	0.99	1.01	0.98	1.02	1.01	1.03	0.98	1.01	0.04	4.0	
Acetaldehyde	2.16	2.22	2.20	2.24	2.26	2.26	2.26	2.26	2.18	2.23	0.04	1.8	
Acrolein	2.03	2.08	2.05	2.08	2.10	2.07	2.08	2.12	2.03	2.07	0.03	1.4	
Acetone	1.96	2.01	2.02	1.99	2.02	2.01	2.00	2.04	1.97	2.00	0.03	1.5	
Propionaldehyde	2.01	2.08	2.06	2.08	2.07	2.12	2.12	2.08	2.04	2.07	0.04	1.9	
Crotonaldehyde	1.97	1.98	1.99	2.03	2.08	2.03	2.01	2.03	1.96	2.01	0.04	2.0	
Butyraldehyde	2.16	2.18	2.19	2.23	2.25	2.24	2.23	2.19	2.21	2.21	0.03	1.4	
Benzaldehyde	2.13	2.20	2.22	2.18	2.20	2.22	2.22	2.20	2.12	2.19	0.04	1.8	

* Concentrations in ng/ μ l.

TABLE 2. RELATIVE RESPONSE FACTORS OF ALDEHYDE
DERIVATIVES (FORMALDEHYDE DERIVATIVE = 1.00)

Compound	Relative Response Factor
Formaldehyde	1.00
Acetaldehyde	1.15
Acrolein	1.28
Acetone	0.79
Propionaldehyde	0.88
Crotonaldehyde	0.82
Butyraldehyde	1.00
Benzaldehyde	1.05
Mean = 1.00	
S.D. = 0.17	

errors in accurately integrating these two peaks. The chromatogram in Figure 3 shows that these two derivatives are not completely resolved.

Several aliquots of the above working standard were shipped to other laboratories equipped with similar sampling and analytical facilities. Two laboratories analyzed the samples, and their results are shown in Table 3, along with Battelle's values. All three laboratories reported very similar concentrations for the formaldehyde and acetaldehyde derivatives. However, laboratory B did not have sufficiently accurate standards for the remaining six DNPH derivatives and chose not to report the data. Battelle and laboratory A showed relatively good agreement for five of the six remaining derivatives. For the crotonaldehyde derivative, Battelle found 2.0 ng/ μ l, while laboratory A reported 1.2 ng/ μ l.

Gas Chromatography

Initially, the gas chromatographic system contained a Megabore fused silica capillary column which was connected to a flame ionization detector. Chromatographic conditions were optimized and several standard mixtures containing the aldehyde derivatives were analyzed. Good linear results were achieved over a range of 0.2 to 20 ng/ μ l. A 3 μ l injection of a 0.2 ng/ μ l formaldehyde derivative standard produced a signal to noise ratio of 3 for the GC/FID system. Unfortunately, a considerable number of contaminant peaks co-eluted with several of the aldehyde derivatives. Some of these peaks were impurities in the DNPH solution, while others were apparently extracted from the screw-capped glass vials used to house the mixtures.

The flame ionization detector was replaced with the electron capture detector to determine if better sensitivity and selectivity could be achieved. Formaldehyde derivative standards were analyzed and again good linear results were achieved over a range of 0.2 to 20 ng/ μ l. A 3 μ l injection of a 0.2 ng/ μ l formaldehyde derivative standard is shown in Figure 4. In viewing the chromatogram, it is evident that the enhanced sensitivity displayed by the ECD should permit the detection of low picogram amounts of the aldehyde derivatives. However, the analysis of the DNPH absorbing solution still reveals numerous contaminants. Additionally, one of the contaminants is only partly separated from the formaldehyde derivative (see Figure 5). A more polar column substrate may facilitate the separation of these two peaks. Likewise, a gas chromatographic system coupled to a mass spectrometer and operated in a mass selective mode may also prove

TABLE 3. RESULTS FROM THE ANALYSIS OF AN EIGHT
COMPONENT STANDARD BY THREE LABORATORIES

Compound (ng/ μ l)	Analysis Laboratory		
	Battelle	Lab A	Lab B
Formaldehyde	1.0	0.9	1.0
Acetaldehyde	2.2	1.9	2.0
Acrolein	2.1	2.1	NA*
Acetone	2.0	1.7	NA
Propionaldehyde	2.1	1.7	NA
Crotonaldehyde	2.0	1.2	NA
Butyraldehyde	2.2	1.6	NA
Benzaldehyde	2.2	2.2	NA

* NA = Not analyzed.

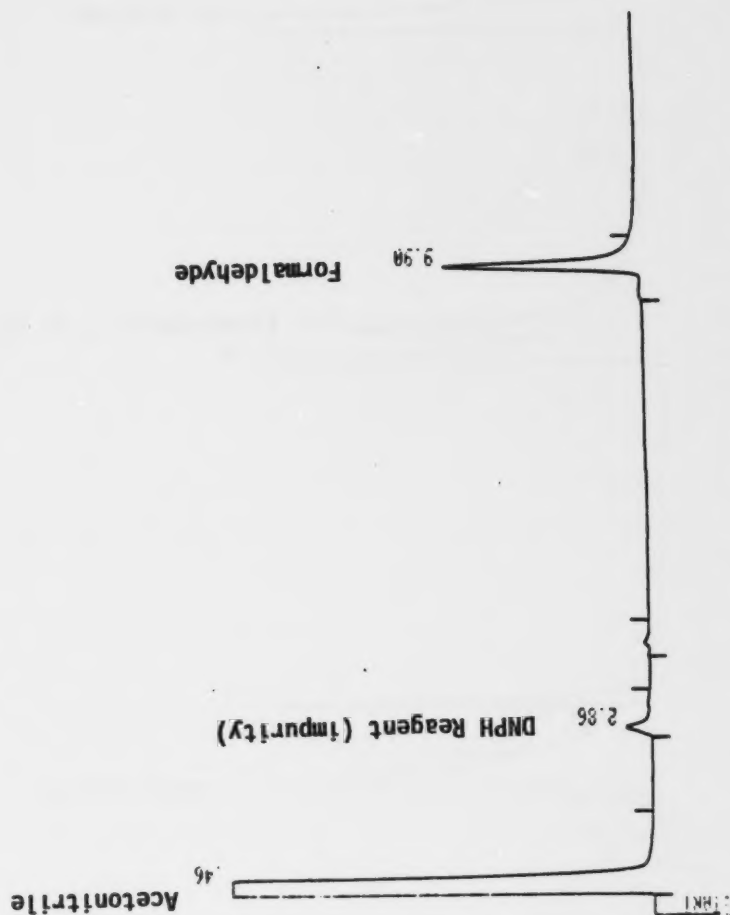


Figure 4. Chromatogram from the injection of 3 μ l of a 0.2 ng/ μ l standard of formaldehyde-DNP derivative in acetonitrile. GC operating conditions are specified in the text.

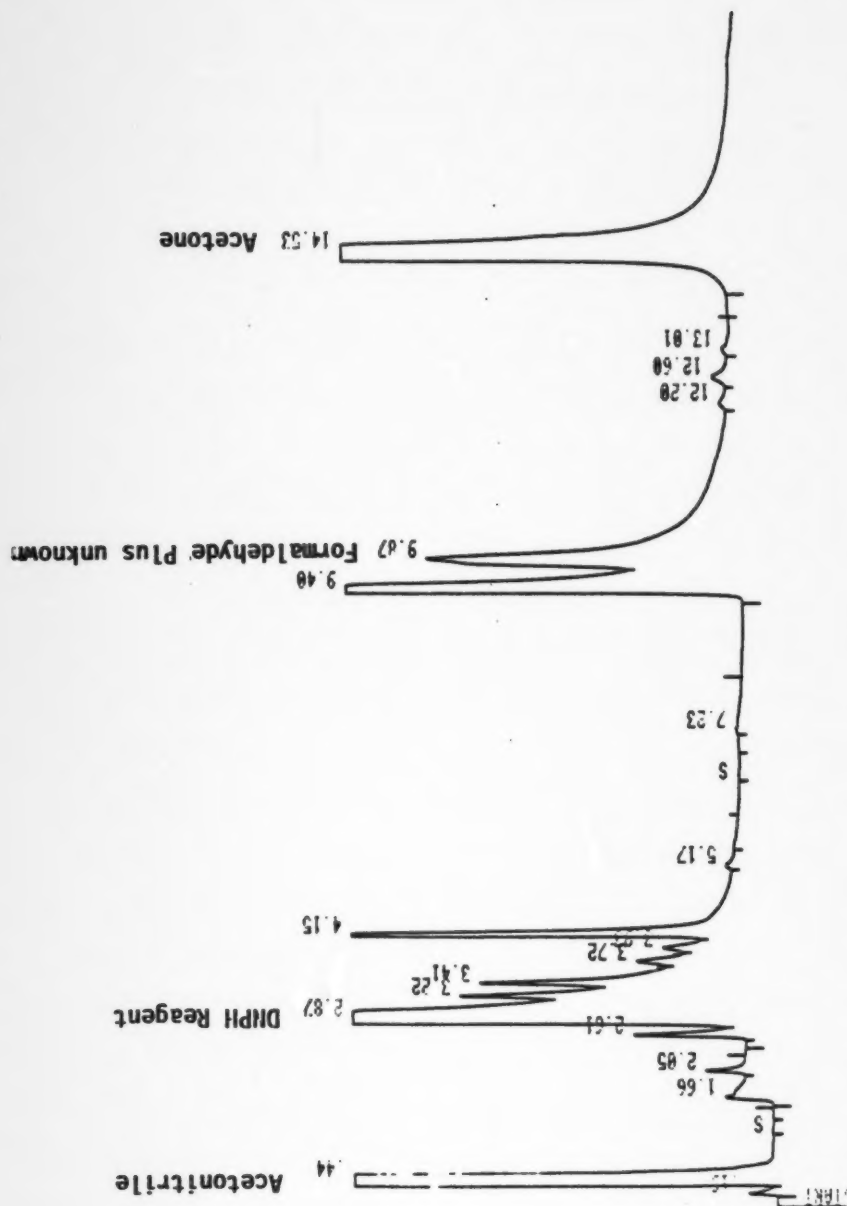


Figure 5. Chromatogram from the injection of 3 μ l of a 0.2 ng/ μ l standard of formaldehyde-DNPH derivative in DNPH/acetonitrile. GC operating conditions are specified in the text.

worthwhile. Investigation of these items were beyond the scope of this study.

CEA Formaldehyde Analyzer

During several test runs with Battelle's 17 m³ environmental chamber, a continuous monitoring analyzer from CEA Instruments, Inc. was evaluated for its sensitivity and selectivity towards ppb levels of formaldehyde. During preliminary tests, liquid formaldehyde standards were prepared and analyzed according to instructions contained in the operator's manual. The results of these analyses are shown in Table 4. The data indicate that, at the instrument's specified flow and calibration set points, excellent agreement is observed between the formaldehyde solution concentrations and the instrument readings.

TABLE 4. RESPONSE OF CEA INSTRUMENT TO
VARIOUS LIQUID STANDARD SOLUTIONS
OF FORMALDEHYDE (ppbV)

Standard Solution	Instrument Reading
0	0
25	21
50	50
125	140
250	250

Following the above tests, the environmental chamber was loaded with various amounts of formaldehyde while monitoring with the CEA analyzer. Cartridge and impinger sampling were also carried out at selected time periods. Additionally, several other aldehydes were added to the chamber at specified times to test the CEA instrument's selectivity toward formaldehyde. The results of these tests are shown in Table 5. The CEA analyzer readings compare very well with the calculated chamber concentrations. At concentrations above 400 ppb, however, the analyzer's response begins to drop off slightly. A plot of calculated chamber concentration versus CEA analyzer reading is shown in Figure 6. The data

TABLE 5. FORMALDEHYDE CONCENTRATIONS FROM TEST METHODS
VERSUS CHAMBER LOADING (ppb)

Calculated Concentration	Method		
	CEA Analyzer	Cartridge	Impinger
5	7	-	-
11	15	-	-
23	26	-	-
57	60 (60)*	59	70
132	128	-	-
221	211 (218)**	175	204
454	382	-	-

* Subsequent addition of acetaldehyde (71 ppb), acrolein (60 ppb), crotonaldehyde (49 ppb), butyraldehyde (45 ppb), and benzaldehyde (39 ppb) did not change instrument response.

** Subsequent addition of acetaldehyde (236 ppb), acrolein (200 ppb), crotonaldehyde (162 ppb), butyraldehyde (149 ppb), and benzaldehyde (131 ppb) resulted in a slight increase in instrument response.

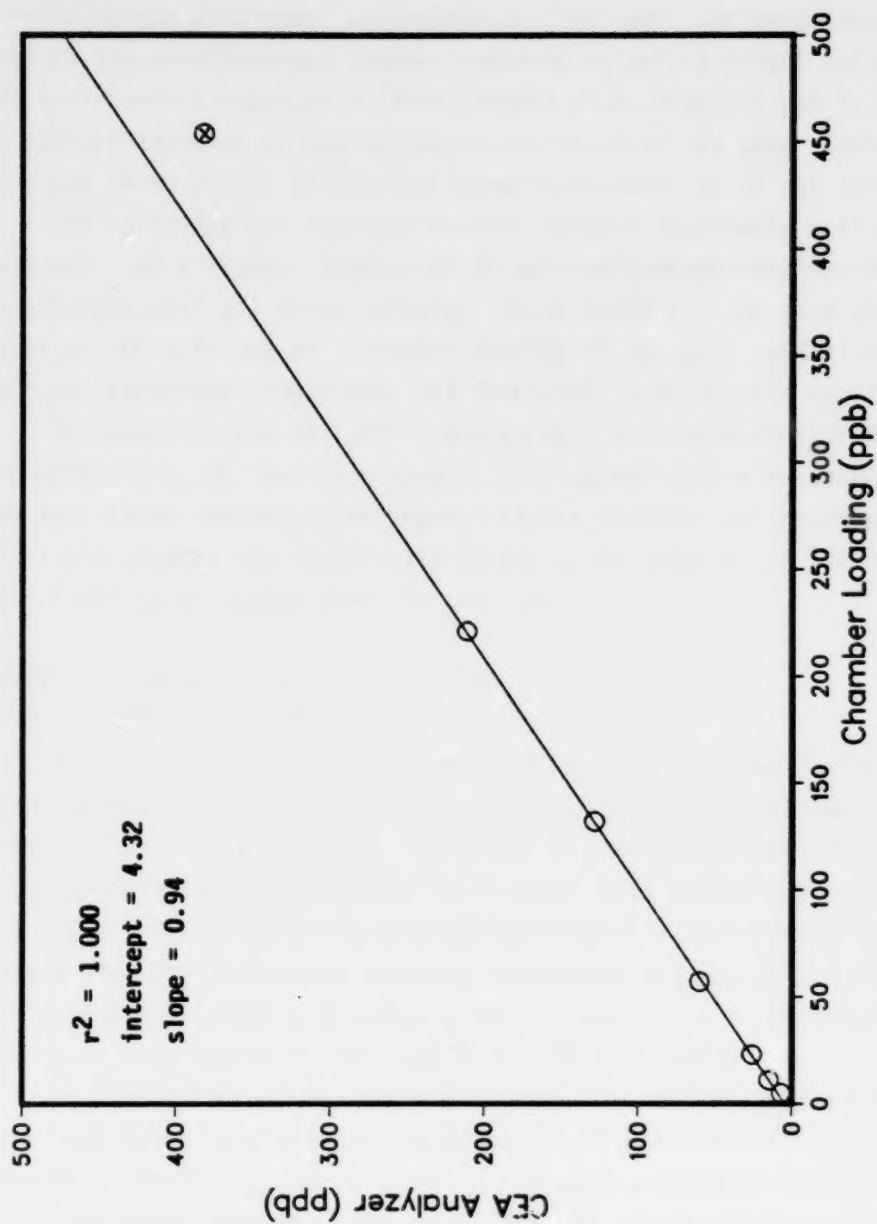


Figure 6. CEA formaldehyde analyzer response to various chamber concentrations of formaldehyde (i.e. formaldehyde was accurately weighed and placed in the chamber).

point at the highest generated concentration was deleted from the calculations and the resulting intercept, slope, and r^2 values are shown on the plot.

The subsequent addition of acetaldehyde (236 ppb), acrolein (200 ppb), crotonaldehyde (162 ppb), butyraldehyde (149 ppb), and benzaldehyde (131 ppb) to the environmental chamber resulted in only a slight increase in the CEA instrument's response to formaldehyde (i.e. from 211 ppb to 218 ppb). An earlier addition of approximately one-third of the same aldehyde mixture resulted in no change in the instrument's response to 60 ppb formaldehyde.

The cartridge and impinger results compare reasonably well with the CEA analyzer. At a chamber loading of 57 ppb, an average reading of 63 ± 6 ppb is obtained with all three methods. These three methods give an average value of 197 ± 19 ppb at a chamber loading of 221 ppb. Additional impinger/cartridge comparisons are discussed later in this section.

Although the CEA analyzer compared very well with chamber loading concentrations, the output response, as measured with a recorder cycles ± 4 ppb at a fixed concentration input. Figure 7 shows the recorder tracing after the chamber was loaded with 23 ppb formaldehyde. An average value of 26 ± 4 ppb is estimated from the tracing.

INVESTIGATION OF STORAGE DEVICES FOR DNPH IMPREGNATED ADSORBENT TUBES

Battelle recently employed DNPH impregnated adsorbent tubes to measure formaldehyde concentrations during a field study in the Kanawha Valley region of West Virginia (17). The mean formaldehyde concentrations ranged from non-detectable to 5.6 ppb. An overall mean concentration of 1.8 ppb was found for the 10 sample runs (24 hr samples--100 liters). However blank levels from the tubes also averaged 1.8 ppb (± 1.4 ppb). The high and variable blank levels are probably due to adsorption of formaldehyde while the tubes were housed in the sample storage containers.

In the present study, various storage devices for DNPH impregnated adsorbent tubes were examined to determine if lower blank levels could be attained. Initially, three types of storage containers were tested: a stainless steel canister pressurized with N_2 , an aluminum can containing a bed of charcoal, and a glass vial with a Teflon lined screw-cap. All adsorbent tubes were prepared in the same manner and stored in the three

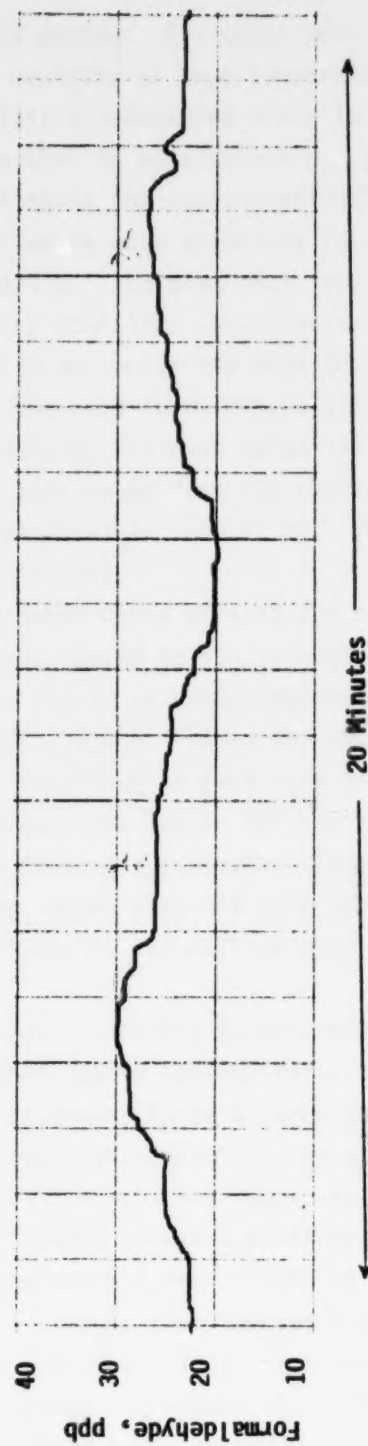


Figure 7. CEA analyzer/recorder response to a chamber loading of 23 ppb formaldehyde.

devices for a five day period. Six tubes were stored together in the pressurized nitrogen canister at room temperature ($\sim 25^{\circ}\text{C}$), six tubes were stored in separate glass screw-capped vials in the refrigerator and six tubes were stored together in an aluminum can containing charcoal at room temperature. Table 6 shows the concentrations found for formaldehyde and acetaldehyde derivatives in each adsorbent tube (ng injected on column) after the five day period. The data show lower amounts of formaldehyde from the tubes stored in the stainless steel canister under a N_2 atmosphere. These values were <0.10 ng, while the mean formaldehyde value from the glass vials is 0.74 ng and the mean formaldehyde value from the aluminum can is 1.32 ng. For acetaldehyde, the mean value from the canister containing N_2 is 0.36 ng while the mean value from the charcoal can is 0.20 ng and the mean value from the glass vials is 0.47 ng. The acetaldehyde differences do not appear to be significant.

To determine if temperature effects are significant, six adsorbent tubes were prepared and stored in separate glass screw-capped vials for five days. Two vials were stored at room temperature, two in the refrigerator and two in the freezer. Table 7 shows the amount of formaldehyde and acetaldehyde derivatives found in each tube (ng injected on column). The formaldehyde and acetaldehyde levels for the tubes stored in the refrigerator and the freezer are somewhat lower than those stored at room temperature. However, there does not seem to be any appreciable difference between storing the tubes in the refrigerator or storing them in the freezer.

Finally, tests were conducted to determine the effect of storage time on blank levels of DNPH coated Sep-Pak cartridges. Two sample batches of the cartridges were studied. Batch A cartridges had been used during earlier tests of storage devices and during subsequent laboratory and field sampling experiments. Batch B cartridges were obtained to determine if there are significant batch to batch differences in blank levels. Six coated cartridges from batch A were stored in a nitrogen-pressurized canister, while 12 cartridges from batches A and B were stored in a second nitrogen pressurized canister. Tubes from each batch were analyzed after 6, 17, and 24 days of storage. A subset of batch A and B tubes were also analyzed immediately after being prepared (i.e. Day 0). Figure 8 shows the formaldehyde and acetaldehyde levels found at each analysis period. At

TABLE 6. RESULTS FROM THE ANALYSIS OF CARTRIDGES STORED IN
THREE DIFFERENT STORAGE CONTAINERS FOR FIVE DAYS

Storage Container/Temperature	Tube #	DNPH Derivatives	
		Formaldehyde (ng on column)	Acetaldehyde (ng on column)
S.S. Canister (N ₂) - (25°C)	1	0.10	0.29
	2	0.10	0.34
	3	0.10	0.49
	4	0.10	0.39
	5	0.10	0.29
	6	0.10	0.34
Glass - (4°C)	1	0.58	0.49
	2	0.87	0.24
	3	0.81	0.24
	4	0.87	0.73
	5	0.75	0.49
	6	0.58	0.58
Aluminum Can (Charcoal) - (25°C)	1	0.81	0.14
	2	0.81	0.14
	3	2.08	0.29
	4	1.33	0.19
	5	1.33	0.19
	6	1.56	0.19

TABLE 7. RESULTS FROM THE COMPARISON OF CARTRIDGES
STORED IN GLASS VIALS UNDER THREE TEMPERATURE
CONDITIONS FOR FIVE DAYS

Temperature Condition	Tube #	DNPH Derivatives	
		Formaldehyde (ng on column)	Acetaldehyde (ng on column)
(25°C)	1	0.98	0.34
	2	1.27	0.39
(4°C)	3	0.92	0.10
	4	0.98	<0.10
(-20°C)	5	1.04	0.10
	6	0.40	0.14

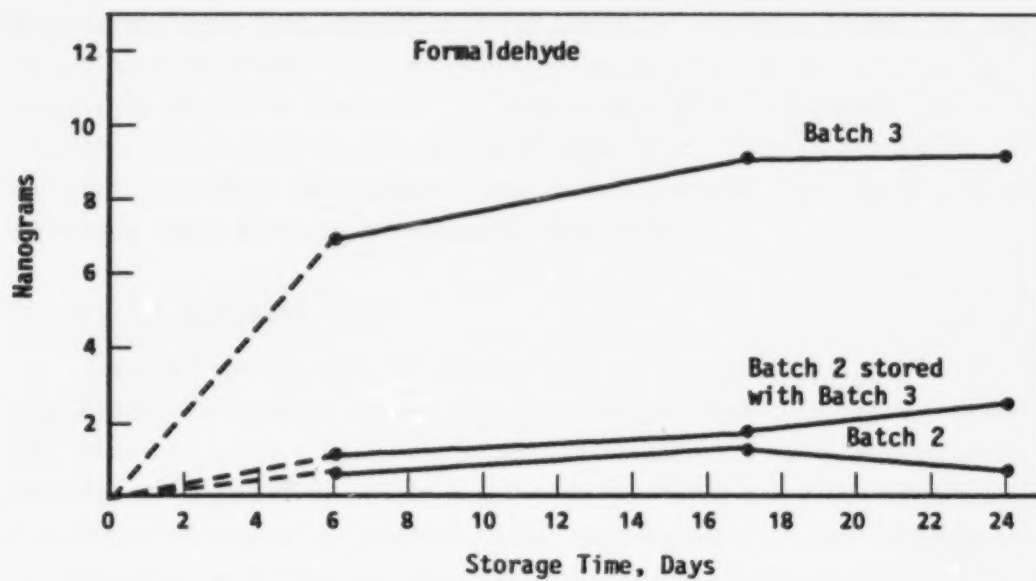
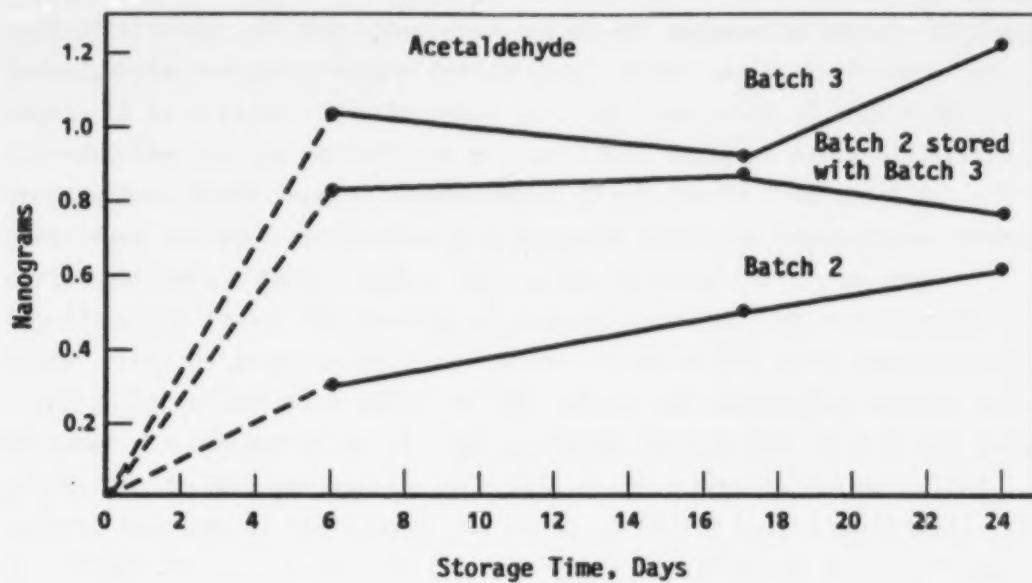


Figure 8. Blank levels of formaldehyde and acetaldehyde derivatives found in various batches of DNPH-coated cartridges.

day 0 no detectable amount of either derivative was observed. After six days of storage, all the tubes analyzed showed measurable amounts of the formaldehyde and acetaldehyde derivatives. After day 6, there does not appear to be a significant increase in blank level with storage time. However, the results do indicate a significant batch to batch difference in formaldehyde blank levels. Formaldehyde blank levels from batch A cartridges averaged approximately 1 nanogram while the levels from batch B cartridges were 8-fold higher. This batch to batch difference may significantly impact the quality of data collected during a monitoring study. For instance, to measure airborne formaldehyde at a concentration of 1 ppb while collecting a 100 liter air sample, the following results are obtained. A concentration of 1 ppb converts to 8.59 ng/L @ 25°C and 1 atm (formaldehyde-DNPH derivative, MW = 210). For a sampled volume of 100 liters, this amount corresponds to 859 ng collected on the cartridge. If 5 ml solvent is used to extract the derivative and 10 µl of the resulting mixture is injected onto the HPLC, then only 1.7 nanograms of the derivative will be measured. With a blank level of 8 nanograms (batch B), efforts to measure airborne formaldehyde at 1 ppb would be in vain. Either the sample volume must be dramatically increased or an alternative batch of coated cartridges should be employed. To assure that quality data will be obtained, batch blank levels should be determined prior to any field monitoring effort. We recommend that blank cartridge level be an order of magnitude lower than the sample cartridge level.

CLEAN UP OF ADSORBENT TUBES

Results from the earlier storage test of Sep-Pak cartridges in nitrogen pressurized containers, showed high formaldehyde levels in batch B tubes and low levels in batch A tubes regardless of whether the tubes were stored together or separately. These results suggest that the formaldehyde contamination source is internal rather than external to the cartridge. The contamination may originate in the silica gel-C₁₈ itself or from the filter plug used to contain the adsorbent. (The manufacturer has indicated that the filter and tube body are made of polypropylene.)

To determine the source of contamination, several of the Sep-Pak cartridges (batch A) were opened and the silica gel-C₁₈ material was removed. Glass, stainless steel and Teflon tubes were then constructed and

packed with the Sep-Pak material. Glass wool was used to contain the adsorbent. Afterward the adsorbent tubes were cleaned and coated with DNPH solution. The cartridges were then stored at room temperature in an aluminum can filled with a layer of charcoal. After five days of storage the cartridges were extracted and analyzed. Formaldehyde and acetaldehyde blank levels were respectively 0.93 ± 0.65 ng and 0.19 ± 0.10 ng ($n = 6$). These blank values are similar to results from earlier studies with the Sep-Pak cartridges (shown in Table 6).

Numerous attempts were then undertaken to clean up the silica gel-C₁₈ material. Several Sep-Pak cartridges were soaked for several days in various solvents (e.g. acetonitrile, hexane, methanol). The tubes were then recoated, stored and analyzed. No improvement in blank levels was observed. Alternative adsorbents, such as silica gel and Tenax, were also tested. Neither performed as well as the Sep-Pak cartridges. Maxiclean cartridges from Alltech were also examined. Blank levels from these tubes were similar to levels from Sep-Pak's batch B cartridges.

SAMPLING/ANALYSIS TEST RUNS

Several test runs were carried out in the laboratory and at field sites in order to evaluate the performance of the Sep-Pak cartridges for collecting airborne aldehydes. Initial laboratory experiments involved spiking aldehyde mixtures onto DNPH-coated cartridges. In addition, Battelle's 17 m³ environmental chamber was utilized to generate target concentrations of various aldehydes. Impinger and cartridge samples were then collected and compared. Field studies focused on outdoor sampling at various suburban locations using cartridge sampling procedures.

Laboratory Experiments

The conversion and recovery of aldehydes on DNPH-coated cartridges were determined by spiking six coated cartridges with 5 μ l of a dilute aldehyde mixture. To facilitate aldehyde impregnation after spiking, 30 L of nitrogen (~ 1 L/min) was passed through the cartridges. The derivatives were then extracted with 5 ml acetonitrile solution. For comparison purposes, 5 μ l of the dilute aldehyde mixture was spiked into 5 ml of the DNPH/acetonitrile working solution. All samples were prepared and analyzed within the same day and the results are shown in Table 8. For five of the

TABLE 8. RECOVERY OF ALDEHYDE DERIVATIVES AFTER SPIKING DNPH-COATED CARTRIDGES (N = 6) WITH AN ALDEHYDE MIXTURE

Aldehyde	Amounted Added (μ g)	Percent Recovered (as DNPH derivative)
Formaldehyde	1.85	96 $\pm$ 5
Acetaldehyde	3.91	93 $\pm$ 8
Acrolein	4.21	84 $\pm$ 10
Crotonaldehyde	4.27	95 $\pm$ 3
Butyraldehyde	4.03	96 $\pm$ 3
Benzaldehyde	5.20	98 $\pm$ 2

six aldehydes, 93-98 percent of the aldehydes were recovered as DNPH derivatives with a 2-8 percent relative standard deviation. Only 84 ± 10 percent of the acrolein was recovered as a DNPH derivative.

The results from the chamber experiments are shown in Tables 9 and 10. During the test runs, the chamber was loaded with six aldehydes at concentrations ranging from 131 to 236 ppb (test run #1) and from 39 to 71 ppb (test run #2). After the chamber was loaded and the injected material had equilibrated, five cartridge samples were collected in parallel over a three hour sampling period. During this time period three 20 minute impinger samples were sequentially collected at evenly spaced time intervals. The average amount of each aldehyde recovered from the five cartridges is given along with the corresponding amount of material found via impinger sampling.

The aldehyde concentrations found with each technique were initially compared with the chamber loading values to determine absolute recovery efficiencies. For both test runs and with either sampling technique, formaldehyde, acetaldehyde, butyraldehyde and benzaldehyde recoveries were generally greater than 80 percent. Considering the concentration levels generated and adsorptive nature of these compounds, the above absolute recovery is quite acceptable. However for acrolein, recoveries ranged from 27 to 44 percent. For crotonaldehyde, recoveries of 124 to 159 percent were found. Both compounds are olefinic aldehydes and it is likely that these species undergo additional chemical reactions during the sampling and analysis process.

Cartridge/impinger ratios for both test runs also compared very well. Ratios ≥ 0.85 were obtained for five of the six aldehydes. Acrolein cartridge/impinger ratios were somewhat lower and averaged 0.72. As the data indicate, however, cartridge sampling results are consistently lower than values obtained from impinger sampling. This difference may be due either to recovery deficiencies with the cartridges or to a sampling bias between methods. Individual cartridge results for both test runs are shown in Tables 11 and 12. The cartridge in position 2 was sampled at a rate three times higher than the remaining four cartridges. If the lower readings from the cartridge samples were due to recovery deficiencies (e.g. breakthrough and/or residence time effects), we would expect that the data from the cartridge in position 2 would be significantly lower than the other

TABLE 9. RESULTS FROM THE ANALYSIS OF CARTRIDGE (Sep-Pak)
AND IMPINGER SAMPLES, CHAMBER TEST NO. 1

Compound	Chamber Loading (ppb)	Cartridge		Impinger		Ratio Cartridge/ Impinger
		Amount Found (ppb)	% Recovered	Amount Found (ppb)	% Recovered	
Formaldehyde	221	174	79	204	92	0.85
Acetaldehyde	236	230	98	230	97	1.00
Acrolein	200	58	29	87	44	0.67
Crotonaldehyde	162	231	143	258	159	0.90
Butyraldehyde	149	120	81	136	91	0.88
Benzaldehyde	131	117	89	120	92	0.98

TABLE 10. RESULTS FROM THE ANALYSIS OF CARTRIDGE (Sep-Pak)
AND IMPINGER SAMPLES, CHAMBER TEST NO. 2

Compound	Chamber Loading (ppb)	Cartridge		Impinger		Ratio Cartridge/ Impinger
		Amount Found (ppb)	% Recovered	Amount Found (ppb)	% Recovered	
Formaldehyde	57	59	104	70	123	0.84
Acetaldehyde	71	70	99	75	106	0.93
Acrolein	60	16	27	21	35	0.76
Crotonaldehyde	49	61	124	67	137	0.91
Butyraldehyde	45	30	67	37	82	0.81
Benzaldehyde	39	33	85	37	95	0.89

TABLE 11. INDIVIDUAL CARTRIDGE RESULTS FROM CHAMBER TEST NO. 1

Compound	Cartridge* (ppbv)					Mean	S.D.	% S.D.
	1	2	3	4	5			
Formaldehyde	174	175	170	175	177	174	2.6	1.5
Acetaldehyde	224	239	228	230	231	230	5.5	2.4
Acrolein	63	88	49	48	44	58	18.0	31.0
Crotonaldehyde	236	259	238	179	243	231	30.4	13.2
Butyraldehyde	124	122	119	119	118	120	2.5	2.1
Benzaldehyde	116	123	114	115	116	117	3.6	3.1

* Cartridge No. 2 was sampled at 300 cc/min for 3 hours, the remaining cartridges were sampled at 100 cc/min for 3 hours.

TABLE 12. INDIVIDUAL CARTRIDGE RESULTS FROM CHAMBER TEST NO. 2

Compound	Cartridge* (ppbv)					Mean	S.D.	% S.D.
	1	2	3	4	5			
Formaldehyde	56	58	61	60	60	59	2.0	3.4
Acetaldehyde	72	69	71	68	69	70	1.6	2.3
Acrolein	23	14	12	10	22	16	5.9	36.9
Crotonaldehyde	63	61	63	59	61	61	1.7	2.8
Butyraldehyde	30	29	30	30	32	30	1.1	3.7
Benzaldehyde	34	32	33	31	35	33	1.49	4.4

* Cartridge No. 2 was sampled at 300 cc/min for 3 hours, the remaining cartridges were sampled at 100 cc/min for 3 hours.

four cartridges. However, this is not the case. Excellent agreement was obtained for all five sampling cartridges. Standard deviation values for four of the six aldehydes were less than five percent. Somewhat higher percent s.d. values were found for the two olefinic aldehydes. (Impinger samples were collected in sequence. No standard deviation calculations were possible because the chamber contents were continually diluted--due to sample volume requirements of the various collection devices.)

During chamber test runs No. 1 and No. 2, DNPH adsorbent tube sampling was carried out with cartridges in tandem. Analyses of the back-up cartridges from both runs were also conducted and shown in Table 13. The aldehyde-derivative values from the back-up cartridges are reported as nanograms on-column for easy comparison with typical blank levels found from DNPH-coated cartridges (Figure 8). The cartridges used in test runs No. 1 and No. 2 were from batch 2. In viewing Table 13 and Figure 8, back-up cartridge levels are very similar to the blank values from batch 2 cartridges.

TABLE 13. RESULTS FROM THE ANALYSIS OF BACK-UP CARTRIDGES FROM CHAMBER TEST RUNS NO. 1 AND NO. 2

Compound	Mean $\pm$ S.D. (n = 10)*
Formaldehyde	1.3 $\pm$ 0.7
Acetaldehyde	0.3 $\pm$ 0.3
Acrolein	0.1 $\pm$ 0.1
Crotonaldehyde	0.3 $\pm$ 0.4
Butyraldehyde	0.2 $\pm$ 0.1
Benzaldehyde	0.2 $\pm$ 0.3

* Values are reported as nanograms on-column.

Field Studies

The purpose of the field study was to determine the utility of the cartridge sampling procedure for measuring amounts of airborne aldehydes. Results from the measurement of aldehydes at one of the suburban locations

are shown in Table 14. Chromatograms from an ambient air analysis and a blank analysis are shown in Figure 9. Twenty-four hour integrated air samples were collected in triplicate with the Sep-Pak cartridges. Flow rates through the three cartridges were maintained at 400, 400, and 700 cc/min respectively. Four blank cartridges were also transported to the field site and were returned for analysis along with the sampled cartridges. Concentrations greater than 0.05 ppbV are reported. For comparison purposes, concentrations from the blanks were calculated using a total "sampled" volume of 576 liters (see equation 1).

Five aldehydes were detected at the site. Formaldehyde was the most predominant species, followed by acetone and acetaldehyde. Acetaldehyde/formaldehyde ratios of ~ 0.3 were found for the two sampling days. Similar airborne aldehyde concentrations and ratios have been reported elsewhere (3). Four of the five measured aldehydes showed standard deviation values less than 10 percent ($n = 3$). Acetone's S.D. values averaged ~ 23 percent. Considering the concentration levels being measured, these values are certainly acceptable. The four blanks showed exceptionally low amounts of aldehydes. When corrected for volume sampled, formaldehyde averaged 0.15 ppb, acetone averaged 0.10 ppb, and the remaining aldehydes were not detected (less than 0.05 ppb). All cartridges were analyzed within 48 hours of preparation. Based upon our earlier discussion, somewhat higher blank levels would have been realized if we had used a more typical two to three week storage time. Nonetheless, the above results indicate that airborne aldehydes can be measured at low ppb levels using the Sep-Pak cartridges and operating under the above stated sampling conditions.

TABLE 14. AIRBORNE ALDEHYDE CONCENTRATIONS AT A SUBURBAN SITE
IN COLUMBUS, OHIO
(24-hour integrated samples collected in triplicate)

Compound (ppbv)*	Site A 8/17/87					Site A 8/18/87				
	Cartridge**			Blank		Cartridge			Blank	
	1	2	3	1	2	1	2	3	1	2
Formaldehyde	5.45	6.15	5.04	0.11	0.17	7.11	7.03	7.00	0.19	0.13
Acetaldehyde	1.49	1.45	1.36	--	--	2.44	2.38	2.28	--	--
Acrolein	--	--	--	--	--	--	--	--	--	--
Acetone	4.05	3.86	2.68	--	0.09	8.08	8.02	4.98	0.12	0.09
Propionaldehyde	0.33	0.37	0.32	--	--	0.56	0.65	0.61	--	--
Crotonaldehyde	--	--	--	--	--	--	--	--	--	--
Butyraldehyde	0.80	0.78	0.62	--	--	2.82	2.78	2.50	--	--
Benzaldehyde	--	--	--	--	--	--	--	--	--	--

	Front Cartridges			Front Cartridges		
	Mean		% S.D.	Mean		% S.D.
	Mean	S.D.	% S.D.	Mean	S.D.	% S.D.
Formaldehyde	5.55	0.56	10.1	7.04	0.06	0.9
Acetaldehyde	1.43	0.07	4.9	2.37	0.08	3.4
Acrolein	--	--	--	--	--	--
Acetone	3.53	0.74	21.0	7.03	1.77	25.2
Propionaldehyde	0.34	0.03	8.8	0.60	0.05	8.3
Crotonaldehyde	--	--	--	--	--	--
Butyraldehyde	0.73	0.10	13.7	2.70	0.17	6.3
Benzaldehyde	--	--	--	--	--	--

* Values less than 0.05 ppb are not reported.

** Cartridge 1 and 2 were sampled at 400 cc/min for 24 hrs (576 liters), cartridge 3 was sampled at 700 cc/min for 24 hrs (1008 liters).

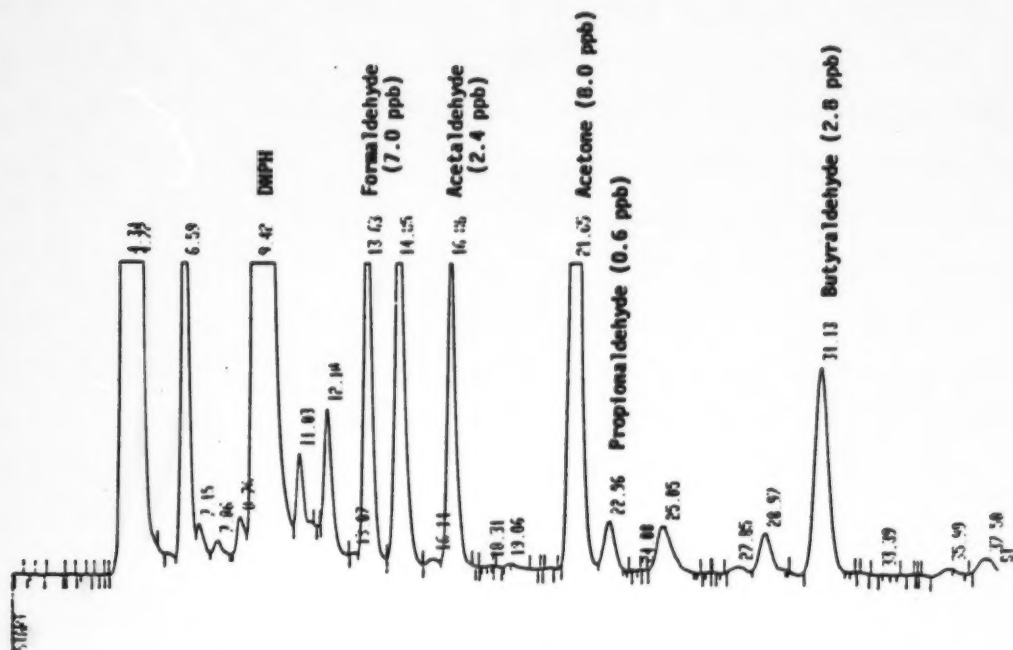


Figure 9A

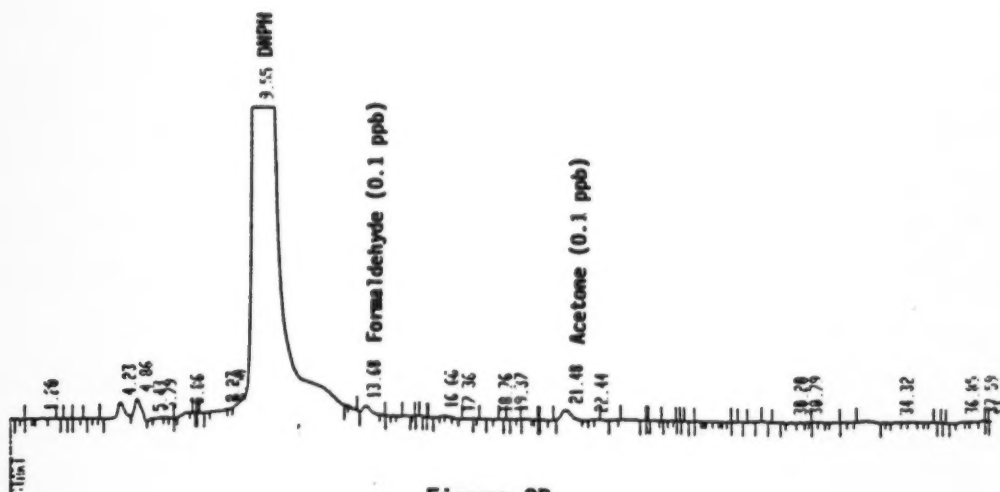


Figure 9B

Figure 9. Chromatograms showing airborne aldehyde concentrations at a suburban site (Figure 9A) along with a corresponding blank analysis (Figure 9B). LC operating conditions are specified in the text.

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